

PATENT SPECIFICATION

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- (21) Application No. 54676/72 (22) Filed 27 Nov. 1972
 (23) Complete Specification filed 22 Nov. 1973
 (24) Complete Specification published 20 Aug. 1975
 (51) INT CL: C08L 77/00; C08K 5/09/(C08L 77/00, 23/02, 23/26)
 (52) Index at acceptance
 C3P 7D1C E2 PC13A PC13C PC20A T2X
 C3R 22C 22D1A2 22D1AX 22D1B2 22D2A2 22D2B2
 22D3D1 22D3DX 22N1A 22N1B C14A C22 C23
 C28X C5B1 C6AX C6X C8P L2CX L6D
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(54) POLYAMIDE/POLYOLEFINE BLENDS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to blends of polyamides and polyolefines and is particularly concerned with improving the compatability of these types of polymers.

According to the present invention there is provided a composition comprising a) at least one polyamide, b) at least one olefine polymer, c) at least one graft copolymer obtained by grafting an unsaturated dicarboxylic acid or the anhydride thereof onto an olefine polymer, and d) at least one compound selected from aromatic carboxylic acids, monocarboxylic acids containing at least one —OH group and which are capable of forming a ring anhydride, polycarboxylic acids containing not more than four carboxylic acid groups and containing not more than one atom of an element other than carbon, hydrogen or oxygen in the molecule and anhydrides of such acids wherein 10—90% of the functions



contained in the acid and/or anhydride groups of components c) and d) are present in the acid or anhydride component of the graft copolymer c), the quantity of the components c) and d) present in the composition is sufficient to provide a total amount of the functions



in the acid and/or anhydride groups equivalent to those provided by between 0.01 and 1.0% by weight of maleic anhydride in the composition, the components a) and b) are each present in an amount of at least 1% by weight, and when component d) is an acid it is present in an amount of not more than the acid equivalent of 0.5% by weight of maleic acid based on the polyamide content of the composition.

The term polyamide as used herein refers to the thermoplastic polymers which are obtained by polycondensation of diamines with dicarboxylic acids, or self-condensation of amino acids or lactams. More particularly it refers to those linear polyamides

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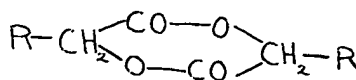
which have fibre-forming characteristics and are termed "nylon". Specifically it includes:

	polyhexamethylene adipamide	(nylon 6:6)	
	polycaprolactam	(nylon 6)	
5	polydodecanolactam	(nylon 12)	
	polyhexamethylene sebacamide	(nylon 6:10)	5
	polyhexamethylene isophthalamide	(nylon 6:iP)	
	polyhexamethylene terephthalamide	(nylon 6:T)	
10	poly-metaxylylene adipamide	(nylon 6:MXD)	
	and copolymers therefrom.		10

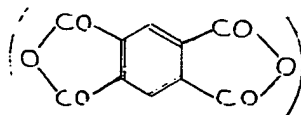
The olefine polymer may include one or more polymerised olefine monomers and suitable polymers of this type include the crystalline polymers of ethylene, propylene, butene-1 and 4-methylpentene-1 and copolymers of these with each other or with other olefine monomers, polymers of propylene and copolymers thereof with up to 25% by weight of ethylene being particularly suitable.

The graft copolymer is conveniently obtained by grafting the unsaturated acid or anhydride onto a polymer of the same olefine as is used as component b) of the composition. The olefine polymer used in c) need not be identical with that used in b) but it is preferred that it is of the same general type, for example both being propylene homopolymers or copolymers of propylene and ethylene. The unsaturated acid or anhydride may be any suitable material which provides a graft copolymer having adhesive properties such as maleic acid, itaconic acid or maleic anhydride.

A wide range of acids, anhydrides or mixtures thereof can be used as component d) of the composition. Thus, component d) can be an aromatic monocarboxylic acid, for example benzoic acid. Monocarboxylic acids containing at least one —OH group and capable of forming a ring anhydride will, for convenience, be referred to as "hydroxymonocarboxylic" acids and it should be appreciated that this term does not include those monocarboxylic acids which contain an —OH group and which are incapable of forming a ring anhydride. The hydroxymonocarboxylic acids used as component d) of the composition may undergo ring formation for example by condensation of two molecules to give a lactide structure of the type



where R is hydrogen, an aliphatic, aromatic or cycloaliphatic group, an acid of this type being for example, lactic acid. The polycarboxylic acids include, di-, tri- and tetra-carboxylic acids, and these may be aliphatic or aromatic, saturated or unsaturated. Acids including hydroxy groups can be used and the acid can include one heteroatom, that is an atom of an element other than carbon, hydrogen and oxygen. Examples of saturated polycarboxylic acids include succinic acid, adipic acid, and citric acid. As unsaturated acids there may be mentioned, for example, maleic acid, fumaric acid, and itaconic acid. Tartaric acid is an example of a polycarboxylic acid which includes at least one hydroxy group, and phthalic acid is an example of an aromatic polycarboxylic acid. Polycarboxylic acids including a hetero-atom include thiodipropionic acid $[\text{S}(\text{CH}_2\text{CH}_2\text{COOH})_2]$ and nitrilotriacetic acid $[\text{N}(\text{CH}_2\text{COOH})_3]$. As anhydrides the anhydrides of the foregoing acids can be mentioned but these may be more, or less, effective than the parent acid. Benzoic, maleic, succinic and phthalic anhydrides are examples of anhydrides of the foregoing acids. As examples of other anhydrides there may be mentioned glutaric anhydride, pyromellitic dianhydride



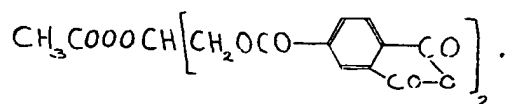
and 'polydride 230', which is a dianhydride having the formula

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The material used as component d) of the composition is preferably stable at the processing temperatures used which are typically in the range 150 to 280°C, and it is particularly desirable that this should be the case if component d) is an acid. If components a) and b) of the composition are used alone, mouldings formed of such a blend have a tendency to delaminate. The compositions of the present invention show an enhanced compatibility and indeed the addition of component d) to a composition containing components a), b) and c) can give improved properties compared to those of the system to which component d) has not been added.

The components c) and d) are conveniently premixed before they are added to the other components of the composition. If component b) of the composition is a propylene polymer, it is very convenient to use a graft copolymer of maleic anhydride and a propylene polymer in admixture with maleic anhydride and/or phthalic anhydride.

It is preferred that from 25 up to 80% of the functions



present in the acid and/or anhydride groups of the components c) and d) are present as the acid and/or anhydride component of the graft copolymer c).

Thus, as a preferred aspect of the present invention there is provided a composition comprising a) at least one polyamide; b) at least one propylene polymer or copolymer thereof with up to 25% by weight of ethylene c) at least one graft copolymer obtained by grafting maleic anhydride onto a propylene polymer or copolymer and d) maleic anhydride and/or phthalic anhydride wherein from 25 up to 80% of the functions



contained in the anhydride groups of components c) and d) are present in the maleic anhydride component of the graft copolymer c), the quantity of the component c) and d) present in the composition is sufficient to provide a total amount of anhydride in the range 0.01 to 1.0% by weight of the composition and the components a) and b) are each present in an amount of at least 1% by weight.

The components a) and b) form the major proportion of the composition and either of these components can be present as the major single component of the composition. If the polyamide is present as the major component, the added olefine polymer (component b)) is effective to reduce the moisture transmission of the polyamide, increase the flexibility and maintain or increase the impact strength of the polyamide. If the olefine polymer is the major component, the added polyamide is effective to improve dyeability and reduce the hydrocarbon vapour transmission of the polyolefine.

We prefer to use compositions wherein the polyamide is the major component, particularly compositions in which the relative proportions by weight of component a) to component b) are in the range 60:40 to 95:5.

Compositions in accordance with the present invention are valuable raw materials which can be processed by the usual methods, for example, by injection moulding, extruding or melt spinning into shaped articles such as threads, fibres, sheets, films and moulded objects such as household articles or machine parts, having a useful combination of properties, such as increased toughness or dyeability, which are derived from both constituent polymers.

The compositions are conveniently prepared using conventional blending techniques such as a high speed powder mixer or a melt mixing technique such as in an extruder or Banbury mixer. The components may be mixed together as a single step but it is preferred to effect the mixing in several stages in order to attain more effective mixing.

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It is convenient to first prepare a mixture of components c) and d). Such a mixture may be prepared by adding a solution of component d) to the graft copolymer and then evaporating the solvent, or by using a solid mixing technique. Alternatively, if the acid and/or anhydride which is component d) is the same as the acid and/or anhydride of the graft copolymer, the blend can be prepared by using an excess of acid and/or anhydride to prepare the graft copolymer, the excess forming the component d). Preparing the blend in this manner the grafting can be carried out using any of the known techniques such as radiation grafting, solution grafting, fluidised bed grafting, or particularly extrusion grafting.

The blend of c) and d) is then mixed with the olefine polymer, for example in a high speed powder mixer, by tumble blending or using a suitable melt mixing technique. The polyamide is then mixed with the blend of the other three components and this mixing is conveniently effected using an extruder.

The compositions of the present invention may also include further additives such as stabilising additives, reinforcing fillers, in particular fibrous materials such as glass fibre, asbestos, carbon fibre, etc., pigments, flame retardants and the like.

The present invention will now be described by reference to the following Examples which are illustrative of the invention but not limiting.

EXAMPLES 1 to 3.

a) Preparation of a blend of graft copolymer and free anhydride.

A blend of maleic anhydride and a graft copolymer of maleic anhydride and a propylene polymer was obtained by mixing together 4 parts by weight maleic anhydride, 100 parts by weight of polypropylene and 1 part by weight of dicumyl peroxide. Grafting was effected using an extruder at 270°C with a residence time of 1½ minutes. The product contained 3% by weight maleic anhydride, of which 1.5% by weight was present in the grafted form and the remaining 1.5% by weight was present as free maleic anhydride.

b) Preparation of a blend of propylene polymer, graft copolymer and free anhydride.

The blend described in a) above was blended with commercially available polypropylene granules (melt flow index measured at 230°C with a 2.16 kgm weight—7.5) in the proportion of 5 or 10% by weight of the blend based on the total weight of propylene polymer and blend. The blending was effected by melt mixing at 200°C in a screw extruder.

c) Preparation of blend of polyamide, propylene polymer, graft copolymer and free anhydride.

Each of the blends prepared in b) was then blended with nylon 66 in varying proportions by adding the nylon and the blends as a chip mix into the hopper of an extruder which was operated at a temperature of 285°C with a screw speed of 60 rpm to give a residence time of 3 minutes. The extruder output was cut into granules and these were injection moulded, in a plunger machine at 280°C, into test pieces for measurement of mechanical properties.

The results obtained and the composition of the various blends are set out in Table I together with some comparative results obtained in the absence of the free anhydride or in the absence of both the free anhydride and the graft copolymer.

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TABLE I

Example or Comparative Example	Ratio Nylon:Propylene Polymer	Blend of c) + d)		Flexural Modulus (2) (psi)	Tensile Strength (3) (psi)	Permanent Elongation after break (4) (%)	Notched Impact Strength (5) (ft lbs/in notch)
		Amount (wt % of total blend)	Type (1)				
1	90:10	0.5	I	3.08 x 10 ⁵	9.5 x 10 ³	70	0.54
2	90:10	1.0	I	3.13 x 10 ⁵	9.5 x 10 ³	58	0.60
3	75:25	2.5	I	2.89 x 10 ⁵	8.4 x 10 ³	42	0.76
A	100:0	NIL	-	3.60 x 10 ⁵	10.7 x 10 ³	75	0.42
B	90:10	NIL	-	3.07 x 10 ⁵	9.0 x 10 ³	20	0.32
C	75:25	NIL	-	2.92 x 10 ⁵	7.4 x 10 ³	8	0.29
D	90:10	0.5	c only	3.00 x 10 ⁵	9.75 x 10 ³	-	0.42
E	90:10	1.0	c only	3.05 x 10 ⁵	9.75 x 10 ³	40	0.42
F	75:25	2.5	c only	2.75 x 10 ⁵	8.32 x 10 ³	28	0.47

(1) Blend I is the graft copolymer plus maleic anhydride.

"c only" means that the graft copolymer only was used, content of grafted monomer 3.6% by weight.

(2) Determined using Method ASTM D790—70.

(3) Determined using Method ASTM D638—68.

(4) Determined by straining a test piece to break and measuring the total elongation of the broken test piece between two points marked on the test piece.

(5) Determined at 25°C using a moulded-in- notch having a notch angle of 45 degrees and a radius at the tip of 0.25 mm using Method ASTM D256—70, Method B.

EXAMPLES 4 and 5.

The general procedure described in respect of Examples 1 to 3 was repeated to obtain compositions containing 75% by weight of the polyamide and 25% of polypropylene containing either 5% or 10% by weight of Blend I. The properties of the compositions are set out in Table II, which also includes the results obtained in the total absence of any additive or in the presence of the graft copolymer only (c only).

TABLE II

Example or Comparative Example	Amount of Blend of c)+d) (% of total blend)	Notched impact (ft.lbs/in. notch)	Flex mod (psi)	Tensile strength (psi)	Elongation at break (%)
4	1.25	0.517	2.87×10^5	7.91×10^3	25
5	2.5	0.754	2.68×10^5	8.06×10^3	60
G	0.625*	0.485	2.77×10^5	7.96×10^3	20
H	1.25*	0.640	2.69×10^5	8.06×10^3	24
I	2.5*	0.744	2.54×10^5	7.96×10^3	28
J	0	0.236	2.63×10^5	7.09×10^3	7

* - c only.

WHAT WE CLAIM IS:—

1. A composition comprising a) at least one polyamide, b) at least one olefine polymer, c) at least one graft copolymer obtained by grafting an unsaturated dicarboxylic acid or the anhydride thereof onto an olefine polymer, and d) at least one compound selected from aromatic carboxylic acids, monocarboxylic acids containing at least one —OH group and which are capable of forming a ring anhydride, polycarboxylic acids containing not more than four carboxylic acid groups and containing not more than one atom of an element other than carbon, hydrogen or oxygen in the molecule and anhydrides of such acids wherein 10—90% of the functions



- contained in the acid and/or anhydride groups of components c) and d) are present in the acid or anhydride component of the graft copolymer c), the quantity of the components c) and d) present in the composition is sufficient to provide a total amount of the functions



- in the acid and/or anhydride groups equivalent to those provided by between 0.01 and 1.0% by weight of maleic anhydride in the composition, the components a) and b) are each present in an amount of at least 1% by weight, and when component d) is an acid it is present in an amount of not more than the acid equivalent of 0.5% by weight of maleic acid based on the polyamide content of the composition.

2. A composition as claimed in Claim 1, wherein the polyamide is polyhexamethylene adipamide; polycaprolactam; polydodecanolactam; polyhexamethylene sebacamide; polyhexamethylene isophthalamide; polyhexamethylene terephthalamide; poly-metaxylene adipamide; and copolymers therefrom.

3. A composition as claimed in Claim 1 or Claim 2 wherein the olefine polymer is a polymer of propylene or copolymer thereof with up to 25% by weight of ethylene.

4. A composition as claimed in any one of Claims 1 to 3 wherein the graft

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- copolymer is one obtained by grafting maleic acid, itaconic acid or maleic anhydride onto a propylene polymer or copolymer.
- 5 5. A composition as claimed in any one of Claims 1 to 4 wherein the material used as component d) is stable at temperatures in the range 150°C to 280°C.
- 10 6. A composition as claimed in any one of Claims 1 to 5 wherein the olefine polymer is a propylene polymer or copolymer, the graft copolymer is one obtained by grafting maleic anhydride onto a propylene polymer or copolymer and component d) is maleic anhydride or phthalic anhydride.
- 10 7. A composition as claimed in any one of Claims 1 to 6 wherein 25 up to 80% of the functions
- $$\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array}$$
- present in the acid and/or anhydride groups of the components c) and d) are present as the acid and/or anhydride components of the graft copolymer c).
- 15 8. A composition as claimed in any one of Claims 1 to 7 wherein the relative proportions by weight of component a) to component b) are in the range 60:40 to 95:5.
- 20 9. A process for the production of a composition as claimed in any one of Claims 1 to 8 wherein components c) and d) are mixed together, this mixture is mixed with the olefine polymer and the polyamide is then mixed with the other three components.
- 20 10. A composition as claimed in Claim 1 and substantially as described in any one of Examples 1 to 5.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
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